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**ABSTRACT:**

Method for producing single crystal ingots continuously by forming a molten body of silicon from two or more feedstocks of silicon, one feedstock containing a predetermined level of dopant, the silicon feedstocks being in the form of solid spheroidal particles of a generally uniform diameter range, continuously drawing a single crystal ingot of doped silicon from said molten body of silicon, said ingot being characterized in that the concentration of dopant is uniform along the length of the ingot, while continuously feeding said feedstocks into said molten body of silicon to thereby maintain constant melt volume and the concentration of dopant uniform throughout the body during the drawing of the single crystal therefrom.



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<b>(21) International Application Number:</b> PCT/US85/00924 <b>(22) International Filing Date:</b> 17 May 1985 (17.05.85) <b>(71) Applicant (for all designated States except US):</b> J.C. SCHUMACHER COMPANY [US/US]; 580 Airport Road, Oceanside, CA 92054 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> SCHUMACHER, John, C. [US/US]; 4533 Cove Drive, Apartment B, Carlsbad, CA 92008 (US). <b>(74) Agents:</b> HUBBARD, Grant, L. et al.; Hubbard, Stetina & Brunda, 24221 Calle de la Louisa, Suite 401, Laguna Hills, CA 92653 (US). <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KP, LU (European patent), MC, NL (European patent),		<b>NO, SE (European patent), SU, US.</b>  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CONTINUOUSLY PULLED SINGLE CRYSTAL SILICON INGOTS  <b>(57) Abstract</b>  Method for producing single crystal ingots continuously by forming a molten body of silicon from two or more feedstocks of silicon, one feedstock containing a predetermined level of dopant, the silicon feedstocks being in the form of solid spheroidal particles of a generally uniform diameter range, continuously drawing a single crystal ingot of doped silicon from said molten body of silicon, said ingot being characterized in that the concentration of dopant is uniform along the length of the ingot, while continuously feeding said feedstocks into said molten body of silicon to thereby maintain constant melt volume and the concentration of dopant uniform throughout the body during the drawing of the single crystal therefrom.		

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## CONTINUOUSLY PULLED SINGLE CRYSTAL SILICON INGOTS

Field of the Invention

This invention relates to semiconductor grade silicon and, more particularly, to a method of producing  
5 large single crystal doped silicon ingots on a continuous basis.

Background of the Invention

Semiconductor grade silicon is a foundational to the large and growing semiconductor, computer, instrumen-  
10 tation and electronic industries. Semiconductor grade silicon is characterized by the requirement of ultrahigh purity, a level of purity not required, and largely unattainable in other fields of chemical and metallurgical technology. Another characteristic of semiconductor grade  
15 silicon is the requirement, in some applications, that the silicon contain minute, but precisely known or controlled amounts of specific impurities. This is known as "doping" silicon, and the product is referred to as "doped" silicon. Exemplary of the elements with which silicon is  
20 doped are boron, phosphorous, arsenic and antimony. Boron is a typical "electron acceptor". Silicon doped in specified areas or throughout a body of silicon with either boron or phosphorous, for example, or with both boron and phosphorous in different regions of the silicon body,  
25 becomes an electron valve, commonly referred to as a semiconductor device, and can perform a great variety of switching, amplification, memory, and other electronic functions in suitable electron control circuits. The semiconductor industry is well developed now, and there  
30 are thousands of semiconductor devices marketed directly, or assembled into computers, radios, televisions, controllers, and nearly an infinite variety of other electronic devices.

Foundational to the semiconductor industry is a  
35 smaller, but still well developed, semiconductor materials supply industry which supplies silicon and silicon compounds, compounds for doping silicon (called "dopants"), and doped silicon, as well as other chemicals,

and a variety of silicon based components in finished, or partially manufactured form.

One form of silicon widely used in the semiconductor industry is the semiconductor grade single crystal silicon ingot. Single crystal silicon ingots, of semiconductor grade, are produced using a very well-known and widely used classical technique for growing single crystals known as the Czochralski method, sometimes referred to as the CZ method. (This method, and various adaptations, are described by Daud and Kachare, "Advanced Czochralski Silicon Growth Technology for Photovoltaic Modules", JPL Publication 82-35, September 15, 1982, DOE/JPL-1012-70.) Single crystal ingots of semiconductor material are grown according to the Czochralski method by contacting a small single crystal of the semiconductor material to be grown with a molten body of the semiconductor material, and drawing the single crystal away from the molten body of the semiconductor material slowly while rotating the single crystal. The single crystal is kept at a temperature lower than the melting point of the crystal. The layer of molten semiconductor material adjacent the crystal, in immediate contact with the crystal, only a few atoms thick, deposits on the single crystal seed, and the seed grows. The atoms of the molten semiconductor material deposit in the same crystal structure as the seed, and, thus, a larger single crystal is formed. This process continues with layer upon layer of single crystal being deposited upon the growing ingot until a large ingot is formed. These ingots may be very large, weighing upward of 100 kg typically, and may be several inches in diameter, and a few feet in length. If the seed and the molten semiconductor material are of high purity semiconductor material, such as semiconductor silicon in the present context, then the result is a single crystal of ultrahigh purity semiconductor grade silicon in which the crystal structure is virtually perfect. A number of

adaptations and variations for growing single crystals are known, see, for example, U.S. Patents Nos. 3,998,598, 4,282,184, 4,410,494, 4,454,096 and 4,458,152. See also "Si Crystal Growth Trends", Semiconductor International, 5 October 1984, pp 55-59.

The Czochralski method is not without limitations however, and while the production of perfect ultrahigh purity silicon is one of technology's crowning achievements, the method is subject to serious problems.

10 The Czochralski method is generally performed as a batch process. A given quantity of silicon from any convenient source is melted in a crucible, and drawn on a seed crystal until the molten semiconductor material is depleted. If the silicon feedstock were perfectly pure, and if there were no impurities introduced in the process, 15 then a perfect single crystal of perfectly uniform purity could, in theory, be produced. Such is not possible, however, and the presence of even minute impurities creates non-uniformity in the ingot purity. As the ingot 20 is drawn from the melt, a phenomenon known as "partitioning" occurs wherein the impurities preferentially migrate into the crystal being grown, or remain preferentially in the melt -- the latter being more common. Typically, the partitioning effect favors build 25 up of impurities in the melt. Thus, as the crystal is grown, the concentration of impurities in the melt increases. Since the partition effect results in a relatively constant percentage of the impurity present in the melt being partitioned into the crystal, as the level 30 of impurity in the melt increases during growth of the crystal, the level of the impurity in the crystal also increases. Thus, the impurity level in the crystal increases as the crystal is grown. (The converse would occur if the impurities partitioned preferentially into 35 the crystal.) In a device in which parts per billion of the impurity can drastically change electronic characteristics, this impurity gradient is a serious problem indeed. This problem is most often overcome by

simply limiting the size of the crystal such that the impurity gradient along the crystal does not significantly effect the electronic characteristics.

It is desirable to produce a single crystal  
5 ingot of silicon which has throughout the crystal a known or controlled amount of dopant, such that the electronic characteristics differ from those of ultrapure silicon, but are uniform at all points along the length of the ingot. It will be apparent from the foregoing that the  
10 Czochralski batch process is not well suited to the production of a uniformly doped single crystal ingot of silicon. A principle feature of the present invention is a method of growing single crystal silicon ingots by a modified Czochralski process on a continuous or semi-  
15 continuous basis wherein the ingots have a uniform level of dopant along the length of the ingot.

Garagaglia, et al., U.S. Patent No. 4,309,241, January 5, 1982, describes the production of silicon by drawing a slim rod of silicon on a seed crystal from a  
20 silicon melt through a chemical vapor deposition chamber to produce an enlarged single crystal semiconductor body. This is a variation of the classical Czochralski method of growing single crystals on a seed crystal; however, in the Garagaglia et al process, the bulk of the silicon  
25 production occurs by vapor decomposition on the surface of the silicon ribbon drawn from the melt, rather from the molten body of silicon.

U.S. Patents 4,036,595 and 4,454,096, Lorenzini, et al., and U.S. Patent 4,282,184, Fiegl, et al., describe  
30 a method for the growth of silicon crystals in which the melt from which the crystals grow is replenished by the transfer of liquid silicon from a replenishment crucible by flow through a transfer tube. This method differs from that of Garagaglia, et al., in that the replenishment of  
35 growing material is via the liquid, and not the vapor.

The production of ultrahigh purity semiconductor grade silicon from tribromosilane is described in U.S. Patent Nos. 4,084,024, Joseph C. Schumacher, April 11,

1978, and 4,328,942, Woerner, et al., March 9, 1982.

Thus, while it is known in the prior art to produce large ingots of silicon semiconductor material, this is done on a batch basis either by the Czochralski method of growing a single crystal from a melt, or by vapor deposition on a heated filament or ribbon of silicon, these processes are limited by the boundary conditions attaching to the batch process, and by the partitioning of impurities. The present invention overcomes these limitations and inadequacies of the prior, and permits the production of ultrahigh purity semiconductor grade silicon ingots, and of ingots of doped silicon having a constant level of doping on a continuous or semicontinuous basis.

Efforts have been made to produce single crystal silicon by the Czochralski method on a continuous basis, but, insofar as is known, no such methods have been found to be fully reliable and completely satisfactory. One of the principal problems with a continuous crystal drawing method of the type described, is that the growth of a high quality, high purity single crystal is very dependent upon maintaining a stable mass and thermal balance in the melt. Even a minor thermal disturbance can upset the crystal growth, and result in a polycrystalline ingot which would normally have to be re-melted as scrap. This, obviously, is a very expensive and undesirable occurrence. The silicon feed stocks of the prior art are typically made up of large or small agglomerations, or chunks of silicon, often of greatly variable size, shape and surface area. Thus, the material is difficult to handle, and cannot be fed into a crucible in a precisely metered manner. The act of providing, or attempting to provide, a continuous feed tends to disturb the CZ furnace heat balance and stability, thus causing or increasing the risk of a defective crystal growth. If the silicon is crushed into fine powder, it acquires an enormous surface area, and acquires substantial impurities simply from the crushing operation. With the large, irregular surface area of such



a product, it is virtually impossible to feed silicon in crushed or comminuted form into a furnace without introducing large amounts of oxygen and other adsorbed and absorbed impurities into the melt. Product quality always suffers, and the risk of large numbers of very expensive rejected ingots is significantly increased. When one considers that a single ingot may be sawed into several thousand wafers, each of which may form from several dozen to several hundred semiconductor devices, or integrated circuits having thousands of semiconductor devices formed therein, the importance of a reliable method of producing perfect single crystal ingots of silicon can be appreciated. An important feature of the present invention is that it solves all, or most of the problems of the prior art respecting continuous growth of silicon ingots, and, thus, opens the way for the economic production of extremely high quality, ultrahigh purity, perfect single crystal silicon ingots on a substantially continuous basis.

#### Summary of the Invention

The present invention may be described as a method for continuously producing semiconductor grade silicon by (a) producing spheroidal, low surface to volume ratio, nonagglomerated individual monodisperse particles of silicon having a diameter of from about 1/2 to about 2 mm, (b) forming a molten body of silicon, (c) continuously feeding the monodisperse particles of silicon of step (a) into the molten body of step (b), and (d) drawing a single crystal of silicon continuously from the molten body of silicon of step (b) to thereby form an ingot of ultrahigh purity silicon having substantially uniform composition along the entire length of the ingot.

The present invention is most advantageous as a method for continuously producing an ingot of silicon having a constant level of doping along the length thereof by (a) forming a body of molten silicon, (b) continuously feeding into said molten body ultrahigh purity spheroidal, low surface to volume ratio, nonagglomerated individual

monodisperse particles of silicon having a diameter of from about 1/2 to about 2 mm, (c) producing spheroidal, low surface to volume ratio, nonagglomerated individual monodisperse particles of silicon containing a  
5 predetermined quantity of dopant and having a diameter of from about 1/2 to about 2 mm, (d) continuously feeding into said molten body the particles of step (c), and (e) continuously drawing a single crystal of silicon having a constant level of dopant from the molten body of dopant  
10 containing silicon to thereby produce an ingot of semiconductor grade silicon having a uniform concentration of dopant therein along the length of the ingot.

The present invention may also be described as a method of producing, on a continuous basis, doped silicon  
15 ingots having constant composition along the length thereof, comprising feeding two streams of spheroidal, low surface to volume ratio, nonagglomerated individual monodisperse particles of silicon into a molten body of silicon, one of said streams being of higher purity than  
20 the other stream, the other stream comprising silicon containing dopant, and continuously pulling a single crystal from the molten body. The invention includes the use of two, three, or more streams of silicon, and doped silicon from several different sources.

25 A principal and important feature of the present invention is the unification of the production of silicon uniquely suited to the production of large, single crystals of silicon, and the actual drawing of such crystals from a melt formed using the uniquely suited  
30 silicon.

The present invention may be described in terms of an overall process comprising the following steps. Tribromosilane is passed, either undiluted or  
35 substantially undiluted, i.e., consisting principally of tribromosilane, through a bed of high purity silicon substrate particles at a reaction temperature in the general range of from about 600 degrees C. to the general range of about 900 degrees C. at about atmospheric

pressure to effect and ensure that thermal decomposition of the tribromosilane onto the substrate particles is carried out. This results in a spheroidal particle product wherein substantially all of the product is in the form of spheroidal (sphere-like) particles having a generally uniform particle diameter in the general range of from about one-half to two millimeters. These spheroidal particles are free flowing, monodisperse, and have a very low surface to volume ratio. As a consequence, the product adsorbs very little moisture, oxygen and other contaminants from the environment. It is easily de-gassed and freed from such limited impurities as are adsorbed on the generally smooth surface thereof.

The next major step (really a series of steps carried out repetitively) is to feed on a generally continuous basis the above-described product at a generally uniform rate into a molten body of silicon from which, directly or indirectly, a single crystal of silicon is drawn. The result is an ultrahigh purity silicon ingot produced very efficiently and economically.

The above process may also include feeding in a number of streams of spheroidal silicon product as described, some or all of which may include a dopant such as boron, antimony, or phosphorous. The nearly uniform, monodisperse spheroidal characteristics of the product permit rather precise control of the rate of feed of each stream of particles and, consequently, permits precise control of the composition of the ingot.

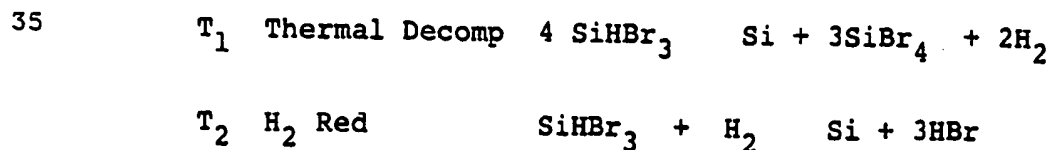
The present invention encompasses the very important and unexpected discovery of a unique form of silicon, and singularly striking and unobvious use of such silicon in a new method for producing perfect single crystal silicon ingots on a continuous basis.

#### Description of the Invention

The Schumacher Silicon Process (SSP), which is described and claimed herein, involves the recognition that a unique form of silicon makes possible a new process with a new result not hitherto known. Semiconductor grade

silicon can be produced in the form of spheroidal, low surface to volume ratio, nonagglomerated individual monodisperse particles of silicon having a diameter of about 1 mm average with a maximum size distribution from about 1/2 to about 2 mm in diameter. This product is a free flowing "shot-like" product with each sphere being very nearly perfect, and approximately the same size as every other sphere. Semiconductor grade as used here is as defined in the semiconductor device fabrication industry, e.g., 0.1 ppb boron, 0.3 ppb phosphorus, etc. This feedstock is formed by thermal decomposition or hydrogen reduction of bromosilanes at 600°C to 1000°C at about atmospheric pressure in a "fluidized bed" reactor to achieve a product diameter from 1/2 millimeter to 2 millimeters. Suitable substrate particles for feedstock to the fluid bed reactor can be created by crushing or attrition of larger particles. The form of the small substrate particles is unimportant - only their purity and freedom from contamination. The spheroidicity of the product of Step 1 of the Schumacher Silicon Process is developed during deposition onto these "substrate" particles fed into the Step 1 fluid bed reactor. The deposition results of course from the thermal decomposition or hydrogen reduction of the bromosilane compound to produce silicon and various by-products depending on the exact bromosilane and decomposition reduction method chosen.

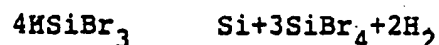
It is critical that sintering be avoided in this step. Sintering avoidance is accomplished in the bromosilane system by its low decomposition temperature, being lowest for thermal decomposition, and raised by hydrogen dilution as a result of some hydrogen reduction, e.g.



$T_2$  being higher than  $T_1$ .

Sintering is a result of surface diffusion under the driving force of surface curvature which causes a distribution of particles to eliminate small particles and grow large particles, reducing the overall, net surface to volume ratio, and binds together the particles in contact with one another to again reduce the system surface/volume ratio.

The thermal decomposition of tribromosilane is effectuated in a reactor within a temperature range of the order of generally 600 degrees C. to 1000 degrees C., and at generally atmospheric or greater pressure. The thermal decomposition is in accordance with the reaction

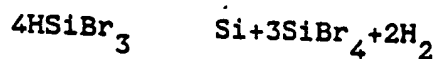


The reactor contains high purity silicon particles which act as substrates for silicon deposition.

The product, ultrapure semiconductor grade silicon, in the form of spheroidal particles, is produced in reactor along with the byproducts hydrogen and tetrabromosilane. The byproducts are recovered and recycled.

The reactor may be a moving bed reactor of the type described in detail in U.S. Pat. No. 4,084,024; or it may be a fluid bed reactor of the type described in U.S. Pat. Nos. 3,012,861; 3,012,862, or 3,963,838.

An important feature of the process of the present invention is the production of ultra-pure semiconductor grade silicon in the reactor at a relatively low temperature lying, for example, within a range of essentially 500 degrees C. to 900 degrees C., without the introduction of hydrogen into the reactor, and without the need for a diluent or for vacuum pressures. The process of the present invention is predicated upon the premise that the chemical reaction



occurs in a temperature range of the order of 600 degrees to 900 degrees C., and at atmospheric pressure 14.7 (PSIA) or above, producing a high yield (80 percent - 100 percent) of purified semiconductor grade silicon deposited on a substrate consisting of fine particles of the purified silicon, and without any tendency to produce amorphous silicon. The monodisperse spheroidal particles are ideal as feed for the next step in the method.

The following example illustrates this facet of the method.

A gaseous stream of tribromosilane is introduced to a fluidized bed reactor which had been filled with 80 mesh silicon. The average core temperature of the reactor is maintained at about 800 degrees C. for about 400 minutes. 0.765 g/min of tribromosilane vapor at 15 PSIA is charged to the reactor. At the completion of the test, spheroidal monodisperse particles of silicon are recovered from the reactor.

The Schumacher Silicon Process (SSP) Step 1 product is monodisperse, it having a size from about 1/2 mm to 2 mm, hence there are no small particles tending to evaporate and deposit on, or grow larger particles that exist in the system. Furthermore, sintering takes place to an appreciable, or noticeable extent at about 60 percent of  $T_{mp}$  °K where  $T_{mp}$  is the melting point of the sintering species for pure, adsorbate-free material. For silicon  $T_{mp} = 1420^\circ\text{C}$  and  $1693^\circ\text{K} \times 0.6 = 1016^\circ\text{K} - 273 = 743^\circ\text{C} = T_{sintering}$ . Thus, at temperatures above about  $750^\circ\text{C}$ , sintering can start to take place. As a particular matter, however, since the Step 1 reactor is a fluid bed reactor, contact times between particles are of a short duration, so that sintering does not become a problem until somewhat higher temperatures, at about  $1000^\circ\text{C} - 1050^\circ\text{C}$  due to this and the monodisperse character of the product.

In Step 2, doped silicon is produced for addition of

donors and acceptors to the continuous CZ melt. Step 2 operates identically to Step 1, except that the bromosilane working fluid employed in the process is not as pure as possible, but is taken from that part of the process where donors or acceptors are concentrated. Make-up working fluid and  $\text{BBr}_3$  or  $\text{PBr}_3$  are added to the feed streams to cause sufficient boron or phosphorus doped polycrystalline silicon of extremely low semiconductor material content (semiconductor grade) to be produced in a fluid bed reactor designated for this purpose.

Step 3 of the SSP is the continuous or semicontinuous production of constant composition single crystal silicon via the CZ process of seed withdrawal from the melt. With current technology which employs batch melting of a specific quantity (5-10 up to 60 or 100 or more kg) of semiconductor grade polycrystalline silicon produced via the Siemens Process, or a fluid bed process which does not utilize bromosilane chemistry and is, therefore, incapable of producing continuous CZ feedstock from Steps 1 and 2, a partitioning of impurities occurs across the solid-liquid phase boundary, since impurities, including donors and acceptors, exist in different equilibrium concentrations in a liquid in equilibrium with its solid phase.

Thus, as the finite quantity "batch" of molten silicon is solidified in the CZ process, concentration of impurities vary with time in the melt and, therefore, with position in the solid solidified from that melt.

In the SSP, this partitioning is avoided for two reasons: (1) It is not a batch process, so that "boundary values" do not interact with operation of the process; and, (2) The melt composition is maintained constant and, therefore, the solid composition is also constant, irrespective of position in the solid (at least in the direction of the "pull" axis).

Constant melt volume is accomplished via addition of feedstock of SSP, Step 1 product, to exactly offset the quantity per unit time removed from the melt via

solidification.

An important feature of the present invention is the step of adding a controlled number of spheroidal, low surface to volume ratio, nonagglomerated individual monodisperse particles of silicon having a mean diameter of about 1 mm to the silicon melt at a constant rate, typically sphere-by-sphere to substantially exactly replenish the melt as the single crystal grows, but without disrupting or disturbing the mass or thermal balance and stability of the crucible or melt. Since the solid feedstock is introduced in particles characterized as spheroidal, thus having the minimum possible surface to volume ratio, and being nonagglomerated individual monodisperse particles of silicon having an approximately uniform diameter of about 1 mm, the effect on the mass of the melt, and upon the heat balance, i.e., the heat required to melt the added silicon and compensate for losses to the single crystal and to the environment, is a function of the rate of introduction of the individual particles. Since the rate of introduction of individual particles, one or more at a time, of substantially identical heat capacity can be controlled and kept constant, there are no disturbances or "spikes" in the heat absorbed in the system or required of the heating source. It is difficult to overestimate the importance of this facet of the invention, as it makes possible the very reliable growth of perfect single crystal silicon on a continuous basis.

Melt composition is maintained essentially constant with respect to the desired constituent of the product ingot doping with additions of SSP using Step 2 product as feedstock.

Thus, the Schumacher Silicon Process comprises the following steps to produce a superior quality wafer for semiconductor device manufacturing, including integrated circuits and silicon photovoltaic solar cells.

1. Prepare a dense, spheroidal monodisperse, large diameter (.5-2 millimeter) semi-



conductor grade polycrystalline silicon shot.

2. Prepare similar sized "doped" polycrystalline silicon shot in the same manner except for addition of species containing dopant reactants to the fluid bed reactor.
3. Add to a CZ melt the product from Steps 1 and 2 to exactly equal silicon and dopant removed from the melt by solidification of single crystal silicon. Here, it is noted that the large size (approximately 1 mm in diameter) of the shot, along with its density, provides a sufficiently low surface to volume ratio to preclude excess oxygen contamination of the melt known to be a problem with older, smaller diameter, and less dense fluid bed products which have attempted to have been used as feedstock for continuous or semi-continuous CZ of semiconductor grade silicon. In addition, the monodisperse nature of the product from Steps 1 and 2 allow the thermal load on the system to be precisely controlled as crystal is withdrawn and shot added to the melt.

An advantage of the process is that it provides an improved quality wafer, as the ingot from which that wafer is sawed must be as uniform as possible. This uniformity is developed by the continuous, or semi-continuous, pulling of CZ crystal from a melt in which constant thermal gradients and constant constitutional gradients exist, and only build up of minor constituents takes place. About 300 ft. of crystal can be pulled prior to too much build up of minor constituents.

As a practical matter, additions to the melt must, in fact, melt prior to coming into contact with the growing solid-liquid interface, so that additions are made behind a weir or other arrangements to provide sufficient time

for such additions to melt, prior to being brought by convection to the region of the growing solid-liquid interface. Alternatively, the spheroidal "shot" may be prevented from striking the solid-liquid surface by proper control of fluid flow patterns in the molten silicon, to cause the shot particles to flow away from the growing crystals.

The weir arrangement is the only feature distinguishing the SSP crucible from ordinary CZ crucibles. The weir, if used, may be circular, concentric with the crystal, or may be in the form of barriers attached to the crucible. Thus, no new equipment, as compared with the CZ crystal drawing equipment, is required. Thus, equipment generally as described in the patents which describe crystal growing techniques and equipment referred to hereinbefore may be used with only minor modification. Crystal may be pulled from a shallow melt, or a deep melt. Various forms of heating, inductive, resistance, R F, microwave, etc. may be used. Electromagnetic fields to control wall contact and melt convection paths may be employed. All of these are known in the art of CZ pulling of single crystal silicon of semiconductor grade.

The apparatus in which SSP is operated may differ from the standard crystal pull furnace only in that arrangement made for handling of the ingot as it is withdrawn from the melt. The standard tower will handle only a limited length ingot. In SSP, an arrangement may be made to keep the crystal aligned to within the critical angle with the melt by side supports which also serve to support the load, at least partially.

The product ingot may then be much longer than typical ingots, and has a much reduced variation with position of both minor and major solute species than conventional CZ ingots. This ingot is then sliced, lapped, and polished into wafers by conventional means. These wafers show little variation in doping, defects, or impurity concentration from one wafer to the next, and

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from one end of the ingot to the other, clearly a vast improvement in the state of the art.

Example 1

Ultrahigh purity monodisperse spheroidal particles of silicon were manufactured according to the process described in U.S. Patent No. 4,318,942. The particles are of high density, of nearly uniform size, from 1/2 to 2 mm and principally about 1 mm in diameter, and formed a free flowing product which was free of fines and dust.

Using the same process, described in U.S. Patent No. 4,318,942, but using as a feedstock tribromosilane containing a controlled concentration of dopant, e.g., boron tribromide or phosphorous tribromide, a product of the same physical appearance, size and characteristics, but with a known, uniform concentration of dopant is produced. The dopant concentration may be at any desired and effective level, generally in the range from 0.001 to 1 ppm, as this product will be used as feedstock to the silicon melt to contribute a low level of dopant. Higher dopant concentrations may be used as well, since any ratio of feedstocks can be used to control the dopant concentration in the silicon melt.

Finally, a body of molten silicon is made up of the desired ratio of feedstocks from the preceeding steps, namely ultrahigh purity silicon and doped silicon, to form a melt of uniform composition. The composition is maintained uniform during the entire operation of the process by continuously feeding in the ratio of feedstocks required. A melt having 5 ppb dopant is maintained by feeding equal quantities of ultrahigh purity silicon, less than 0.1 ppb, and doped silicon having 10 ppb dopant. A single crystal of silicon, which may be of ultrahigh purity, is contacted into the melt and withdrawn while being rotated, according to the classical Czochralski technique, thus growing a single crystal ingot having a uniform composition along the entire length of 5 ppb. The single crystal may be drawn continuously from the melt for

very long periods of time. Calculations indicated that a single crystal up to 300 feet long is entirely feasible, although equipment design and handling convenience suggest that a crystal of this length may not be efficiently handled.

In summary, the method of this invention comprises producing single crystal ingots continuously by forming a molten body of silicon semiconductor material of two feedstocks of silicon, one feedstock containing a predetermined level of dopant; continuously drawing a single crystal ingot of doped silicon from said molten body of silicon, said ingot being characterized in that the concentration of dopant is uniform along the length of the ingot, while continuously feeding said feedstocks into said molten body of silicon to thereby maintain the concentration of dopant uniform in said body during the drawing of the single crystal therefrom. The term continuous, or continuously, as used herein means carrying out the process while repeating the steps set forth either periodically, or without interruption. Thus, a continuous process, sometimes referred to as semi-continuous, would involve the repeated periodic introduction of silicon material feedstock while the crystal was being drawn from the melt, as well as constantly adding silicon material feedstock during drawing of every feedstock. Every feedstock inherently contains some impurity or additive, hence, the terms ultrapure silicon and doped silicon are used in the normal technical meaning of these terms. The two feedstocks could, within the scope of the invention, contain, respectively, two concentrations of the same dopant or concentrations, the same or different, of two or more dopants.

The method of the invention, then, may be described as including the steps of feeding a first feedstock into a molten body of silicon semiconductor material, said first feedstock comprising ultrahigh purity semiconductor grade silicon; feeding a second feedstock comprising ultrahigh purity semiconductor grade silicon to

which a known amount of semiconductor dopant has been added; and, while carrying out the above-stated steps, drawing a single crystal of doped silicon from said molten body. The method of the invention preferably includes the

5 steps of introducing into said molten body a first silicon composition characterized in being spheroidal, low surface to volume ratio, nonagglomerated individual, monodisperse silicon particles having a diameter of about 1 mm, and introducing into said molten body a second silicon

10 composition characterized in being spheroidal, low surface to volume ratio, nonagglomerated individual, monodisperse doped silicon particles having a diameter of about 1 mm, and carrying out these steps while drawing from the molten body an ingot of doped silicon of semiconductor grade.

15 The doped silicon particles preferably contain boron, antimony, arsenic, or phosphorous. In a particularly beneficial form of the invention, the silicon particles and the doped silicon particles have a mean diameter of about 1 mm, and the particle feedstocks are substantially

20 free of sintered particles, particles substantially over 2 mm in diameter, and fine particles substantially under 1/2 mm in diameter.

#### Industrial Application

This invention finds wide and general

25 application in the semiconductor industry.

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## WHAT IS CLAIMED IS:

1. The process of producing single crystal ingots continuously comprising the steps of:

(a) forming a molten body of silicon semiconductor material of two feedstocks of silicon, one feedstock containing a pre-determined level of dopant;

(b) continuously drawing a single crystal ingot of doped silicon from said molten body of silicon, said ingot being characterized in that the concentration of dopant is uniform along the length of the ingot; while

(c) continuously feeding said feedstocks into said molten body of silicon to thereby maintain constant melt volume and the concentration of dopant uniform in said body during the drawing of the single crystal therefrom.

2. The method comprising the steps of:

(a) feeding a first feedstock into a molten body of silicon semiconductor material, said first feedstock comprising ultrahigh purity semiconductor grade silicon;

(b) feeding a second feedstock into the aforesaid molten body of silicon, said second feedstock comprising ultrahigh purity semiconductor grade silicon to which a known amount of semiconductor dopant has been added; and

(c) while carrying out steps (a) and (b), drawing a single crystal of doped silicon from said molten body, steps (a), (b) and (c) being carried out on a substantially continuous basis.

3. The method of growing single crystal silicon comprising the steps of:

(a) forming a molten body of silicon of semiconductor grade;

(b) introducing into said molten body a first silicon composition characterized in being

spheroidal, low surface to volume ratio, non-agglomerated individual, monodisperse silicon particles having a diameter of about 1 mm;

5 (c) introducing into said molten body a second silicon composition characterized in being spheroidal, low surface to volume ratio, nonagglomerated individual, monodisperse doped silicon particles having a diameter of about 1 mm; and

10 (d) substantially continuously carrying out steps (b) and (c) while drawing from said molten body on a substantially continuous basis an ingot of doped silicon of semiconductor grade.

4. The process of Claim 3 wherein the doped  
15 silicon particles contain boron, antimony or phosphorous.

5. The process of Claim 3 wherein the silicon particles of step (b) and the doped silicon particles of step (c) have a mean diameter of about 1 mm and the particle feedstocks are substantially free of sintered  
20 particles, particles substantially over 2 mm in diameter and fine particles substantially under 1/2 mm in diameter.

6. The process of growing single crystal silicon ingots comprising the steps of:

(a) forming a molten body of silicon;  
25 (b) drawing from said molten body a single crystal ingot of silicon; and

(c) introducing into said molten body at a controlled rate to make up silicon drawn therefrom individual silicon particles  
30 characterized as spheroidal, low surface to volume ratio, nonagglomerated individual monodisperse particles of silicon having a diameter of from about 1/2 to about 2 mm.

7. The continuous process of growing single  
35 crystal silicon ingots comprising the steps of:

(a) forming a molten body of silicon;  
(b) introducing substantially continuously into said molten body at a controlled rate,

individual silicon particles characterized as spheroidal, low surface to volume ratio, nonagglomerated individual monodisperse particles of silicon having a substantially uniform diameter; and

(c) drawing a single crystal ingot of semiconductor grade silicon from said molten body substantially at the rate at which silicon is introduced by way of the aforesaid particles.

8. The process of Claim 6 comprising the further step of:

(d) introducing into said molten body at a controlled rate, individual silicon particles differing from the first said particles characterized as spheroidal, low surface to volume ratio, nonagglomerated individual monodisperse particles of silicon containing dopant having a substantially uniform diameter.

9. The process comprising the steps of:

(a) passing tribromosilane through a bed of high purity silicon substrate particles at a reaction temperature in the range of from about 600° C. to about 900° C. at about atmospheric pressure to effect thermal decomposition of the tribromosilane onto the substrate particles forming a spheroidal product particles having a generally uniform particle diameter of from about one-half of two millimeters, the said particles being free flowing, monodisperse and having a very low surface to volume ratio;

(b) forming a molten body of silicon;

(c) introducing into said molten body at a controlled rate to make up silicon drawn therefrom individual silicon particles from step (a).

10. The process comprising the steps of:

(a) passing tribromosilane through a bed of high purity silicon substrate particles at a



reaction temperature in the range of from about 600° C. to about 900° C. to effect thermal decomposition of the tribromosilane onto the substrate particles forming a spheroidal product particles having a generally uniform particle diameter of from about one-half to two millimeters, the said particles being free flowing, monodisperse and having a very low surface to volume ratio;

(b) forming a molten body of silicon;

(c) introducing substantially continuously into said molten body at a controlled rate, individual silicon particles from step (a);

(d) drawing a single crystal ingot of semiconductor grade silicon from said molten body substantially at the rate at which silicon is introduced by way of the aforesaid particles.

11. The process of Claim 10 comprising the further step of:

(d) introducing into said molten body at a controlled rate, individual silicon particles differing in composition from the first said particles.

12. The process comprising the steps of:

(a) passing tribromosilane through a bed of high purity silicon substrate particles at a reaction temperature in the range of from about 600° C. to about 900° C. to effect thermal decomposition of the tribromosilane onto the substrate particles forming a spheroidal product particles having a generally uniform particle diameter of from about one-half to two millimeters, the said particles being free flowing, monodisperse and having a very low surface to volume ratio;

(b) passing tribromosilane and a dopant through a bed of high purity silicon substrate particles at a reaction temperature in the range

of from about 600° C. to about 900° C. to effect thermal decomposition of the tribromosilane onto the substrate particles forming a spheroidal product particles of doped silicon having a generally uniform particle diameter of from about one-half to two millimeters, the said particles being free flowing, monodisperse and having a very low surface to volume ratio;

(c) drawing a crystal from a body of molten silicon;

(d) feeding a stream of particles from step (a) and a stream of particles from step (b) into the body of molten silicon.

# INTERNATIONAL SEARCH REPORT

International Application No **PCT/US85/00924**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <b>INT. CL.3 C30B15/12; C01B 33/02, 33/08</b> <b>U.S. CL. 156/601,605,617SP, Dig64; 423/349</b>						
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>4</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border: 1px solid black; text-align: left;">Classification System</th> <th style="border: 1px solid black; text-align: left;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; vertical-align: top; padding: 5px;"><b>US</b></td> <td style="border: 1px solid black; padding: 5px;">156/605,617SP,624, Dig.64, Dig.88; 423/349; 427/86, 213, 215; 51/307</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>4</sup></div>			Classification System	Classification Symbols	<b>US</b>	156/605,617SP,624, Dig.64, Dig.88; 423/349; 427/86, 213, 215; 51/307
Classification System	Classification Symbols					
<b>US</b>	156/605,617SP,624, Dig.64, Dig.88; 423/349; 427/86, 213, 215; 51/307					
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>						
Category <sup>9</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>				
Y	US,A, 3,012,862, PUBLISHED 12 DECEMBER 1961, BERTRAND ET AL.	8-12				
Y	US,A, 3,012,861, PUBLISHED 12 DECEMBER 1961, LING.	8-12				
Y	US,A, 4,282,184, PUBLISHED 04 AUGUST 1981 FIEGL ET AL.	1-12				
Y	US,A, 2,892,739, PUBLISHED 30 JUNE 1959, RUSLER.	1-12				
Y	DE,A1, 2,704,043, PUBLISHED 20 JULY 1978	1-12				
Y	US,A, 2,938,772, PUBLISHED 31 MAY 1960, ENK ET AL.	8-12				
Y	US,A, 4,318,942, PUBLISHED 09 MARCH 1982, WOERNER ET AL.	8-12				
Y	US,A, 4,036,595, PUBLISHED 19 JULY 1977, LORENZINI ET AL.	1-12				
Y	US,A, 4,084,024, PUBLISHED 11 APRIL 1978, SCHUMACHER.	8-12				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>*</sup> Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"4" document member of the same patent family</p> </div> </div>						
<b>IV. CERTIFICATION</b>						
Date of the Actual Completion of the International Search <sup>3</sup>  <div style="text-align: center; font-weight: bold;">08 JULY 1985</div>		Date of Mailing of this International Search Report <sup>3</sup>  <div style="text-align: center; font-weight: bold; font-size: 1.2em;">23 JUL 1985</div>				
International Searching Authority <sup>1</sup>  <div style="text-align: center; font-weight: bold;">ISA/US</div>		Signature of Authorized Officer <sup>10</sup> <div style="text-align: center;"> <b>DAVID LACEY</b> </div>				